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Predicting the Radiation Tolerance of Oxides

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We have used atomistic computer simulations and ion beam irradiations to examine radiation damage accumulation in multi-component oxides. We have developed contour energy maps via computer simulations to predict the effects of oxide structure and chemical composition on radiation-induced atomic disorder, defect migration, and swelling. Ion irradiation damage experiments have been performed on, pyrochlore and fluorite-structured oxide ceramics to test the predictions from computer models.

Keywords: radiation damage, oxides, pyrochlore, fluorite

1. Introduction

In the simplest description of radiation damage, irradiation produces an enhanced concentration of Frenkel defect pairs (elevated relative to the thermal equilibrium concentration), which leads to increased crystal energy. Both chemical and topological disorder accompany point defects in a lattice such as a complex oxide and this disorder leads to static atomic displacements. In one model for irradiation-induced amorphization, an amorphous transformation occurs when the sum of the thermal and static atomic displacements reaches a critical value (an extension of the Lindemann criterion for solid state melting).¹⁾ In this context, a material that exhibits significant radiation tolerance would be one in which either the enthalpy stored in the lattice due to atomic defects is particularly low, or the critical static displacement level that the lattice can endure is unusually high. Such materials are expected to resist amorphization.

The stored energy associated with lattice defects can also be reduced by (1) Frenkel pair recombination (annihilation) or (2) point defect aggregation into extended defects such as dislocation loops and pores. The latter is a localized secondary response to primary displacements and leads to irreversible incorporation of new atom sites and concomitant swelling. This response to irradiation is no more desirable than is amorphization.

Ideally, a radiation tolerant material will (1) possess an ability to accommodate point defects with minimal stored energy and (2) be able to suppress the action of point defect aggregation mechanisms, by comparison to the mechanism of point defect recombination. The latter property has been found in materials that possess complex chemistries and structures, and is believed to be due to constraints that complex chemistry and structure place on the nucleation and growth of dislocation loops.^{2,3)} For this reason, we have concentrated our work on complex oxides and on the ability of such oxides to accommodate point defects in their lattices. Moreover, we have considered oxides with high ionicities. This is because previous studies have demonstrated a correlation between ionicity and amorphization resistance in both simple⁴⁾ and complex⁵⁾ oxides. In this paper, we will concern ourselves only with (3+, 4+) pyrochlore oxides with formula $A_2^{3+}B_2^{4+}O_7$. Pyrochlores are model complex oxides, ideally suited to testing the relationships between atomic disorder and radiation tolerance.

2. Experimental Procedure

We performed atomistic computer simulations to determine the detailed crystal structure of (3+, 4+) cubic pyrochlore compounds.⁶⁾ We considered cations ranging from lanthanum to lutetium on the A site and titanium to cerium on the B site. Our approach allowed us to study not only the perfect crystal

lattice, but also to predict the extent to which a given lattice accommodates point defects. Our goal was to develop a quantitative understanding of the trends involved in cation disorder, cation and anion Frenkel disorder, and the interdependence of these disorder mechanisms, as a function of A and B cation radii.

We tested the lattice stability predictions from computer simulations by performing ion irradiation experiments on selected pyrochlore and fluorite compounds. Samples were irradiated under cryogenic conditions ($T \sim 120\text{K}$) using 350 keV Xe^{++} ions to fluences ranging from 1×10^{15} to 5×10^{16} Xe/cm^2 . Irradiated samples were then prepared in cross-section for analysis using transmission electron microscopy (TEM).

3. Results and Summary

Figure 1 shows a contour plot of the calculated formation energy for isolated defect complexes in a wide range of (3+, 4+) $\text{A}_2\text{B}_2\text{O}_7$ compounds. The specific defect complex considered here consists of a cation antisite (via reaction $\text{A}_{\text{A}(16\text{d})} + \text{B}_{\text{B}(16\text{c})} \longrightarrow \text{A}_{\text{B}(16\text{c})} + \text{B}_{\text{A}(16\text{d})}$) along with an anion Frenkel (via reaction $\text{O}_{\text{O}(48\text{f},8\text{b})} \longrightarrow \text{V}_{\text{O}(48\text{f},8\text{b})}^{\bullet\bullet} + \text{O}_{\text{i}(8\text{a})}$). This point defect cluster occurs with the lowest energy expense compared to all other point defect reactions considered in our study.⁶⁾ It is interesting to note that combining the above reactions produces a local transformation from an ordered pyrochlore into a disordered fluorite structure. The cation antisite and anion Frenkel defect reactions are consistent with typical point defects generated in a displacive radiation environment. The plot in Fig. 1 indicates that cation antisite and anion Frenkel defect formation is accompanied by high energy cost in compounds containing large A cations and comparatively smaller B cations. The lowest defect energies are associated with compounds in which A and B radii are more similar. As cation antisite defects and anion Frenkels are an inevitable consequence of a displacive radiation

environment, Fig. 1 can also be interpreted as a predictor of radiation damage behavior: compounds with highly dissimilar cationic radii, $r(\text{A}^{3+}):r(\text{B}^{4+})$, should exhibit the greatest susceptibility to lattice destabilization (and possible amorphization), while compounds with similar $r(\text{A}^{3+}):r(\text{B}^{4+})$ should behave more robustly in a radiation environment.

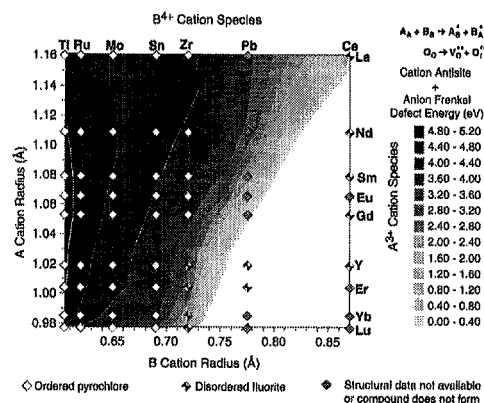


Fig. 1. Contour map showing the calculated isolated defect complex formation energy (complex consisting of a cation antisite plus an anion Frenkel) for a variety of compounds with $\text{A}_2\text{B}_2\text{O}_7$ stoichiometry. A cations are arranged in order of increasing radii along the ordinate; likewise for B cations on the abscissa (ionic radii based on Shannon⁷⁾). For each compound, calculations were performed assuming a pyrochlore cubic unit cell containing eight formula units. Not all compounds indicated here are known to form pyrochlores. Experimentally confirmed pyrochlores are indicated with open symbols, while checked symbols represent compounds known to form fluorites. For compounds labeled with gray symbols, structural data was not available or the compounds have not been observed experimentally.

Fig. 1 also shows that compounds with more similar cation radii are more likely to form as disordered fluorites than as ordered pyrochlores, because the energy expended to form the kinds of defects that cause an ordered pyrochlore to resemble a disordered fluorite (cation antisites and anion Frenkels) is far lower for compounds of similar cation radii, compared with compounds containing A and B cations with

highly disparate sizes. The symbols used in Fig. 1 to represent the 'observed' structure of $A_2B_2O_7$ compounds, illustrate that the 'as-synthesized' structure of these oxides is consistent with the defect energy map that we have generated for these (hypothetical) ordered pyrochlore compounds.

We have performed ion irradiation damage experiments on selected $A_2B_2O_7$ compounds, to test the predictive capabilities of our atomistic simulation results in terms of radiation damage behavior. We demonstrated that a rare-earth zirconate (a disordered fluorite as-synthesized) is less perturbed by irradiation than a similar titanate (titanates are highly-ordered pyrochlores).⁸⁾ This is not so surprising when one considers that before exposure to ions, the zirconate resembled an irradiated compound. We have since demonstrated that rare-earth cerates are also exceptionally resistant to amorphization under ion irradiation.⁹⁾ These results seem to correlate favorably with predictions that we infer from the calculation results in Fig. 1. We are now in the process of testing the methodology that we have developed here, to predicting the radiation response of complex oxides with other crystal structures. For instance, we are examining both theoretically and experimentally the behavior of (3+, 3+) perovskite oxides with formula $A^{3+}B^{3+}O_3$. These studies should help us to assess the possible 'universality' of the concepts we have developed in the study presented here.

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